LA-UR- 02-6481

Approved for public release; distribution is unlimited.

Title: SIMULATION OF RADIOLYSIS IN THE NEAR FIELD OF A NUCLEAR REPOSITORY AND THE SPECTROPHOTOMETRIC INVESTIGATION OF THE FORMATION OF RADIOLYSIS BY-PRODUCTS BY APPLYING HIGH ENERGY BEAM-LINE EXPERIMENTS

Author(s): T. HARTMANN, P. PAVIET-HARTMANN, C. WETTELAND, N. LU, D. WARE, S. SAGE

Submitted to: MRS 2002 Conference, December 2-6, 2002, Boston, MS

Los Alamos
NATIONAL LABORATORY

12,38,58

SIMULATION OF RADIOLYSIS IN THE NEAR FIELD OF A NUCLEAR REPOSITORY AND THE SPECTROPHOTOMETRIC INVESTIGATION OF THE FORMATION OF RADIOLYSIS BY-PRODUCTS BY APPLYING HIGH ENERGY BEAM-LINE EXPERIMENTS

T. HARTMANN, P. PAVIET-HARTMANN, C. WETTELAND*, N. LU**, D. WARE**, S. SAGE***
Los Alamos National Laboratory, Earth and Environmental Science Division, Los Alamos, NM 87544, USA (hartmann@lanl.gov)
*Los Alamos National Laboratory, Materials Science Division, Los Alamos, NM 87544
** Los Alamos National Laboratory, Chemistry Division, Los Alamos, NM 87544
*** CEMRC, Carlsbad, NM 88220

ABSTRACT

In the event of inundation of a nuclear waste repository located in a geological salt formation, chloride brines in contact with nuclear waste will be exposed to different kind of radiation depending on waste-form conditions. Ionizing radiations, however, have the ability to significantly affect the groundwater chemistry of the brines through the formation of free radicals, ionic- and molecular species; among them the typical by-products of α-radiolysis: hypochlorite (OCl^-) and hypochlorous acid (HOCl). In the absence of effects which are supposed to dominate the redox conditions in the repository (corrosion of metals, microbial activity) the presence of OCl^- is known to increase the redox potential of the brines and further to influence the stability of actinide waste-forms by accelerating their dissolution and - most importantly – to oxidize actinides to their higher oxidation states, which are generally the most soluble ones.
We are presenting a new approach to determine the radiation-induced formation rates of hypochlorite and hypochlorous acid as a first step to assess long-term steady-state repository conditions. To overcome the serious constraints of conventional radiochemical work with GBq activity levels, we are simulating α-irradiation of chloride brines by the adaptation of ion-beam-line experiments. Therefore, we irradiate liquid chloride brine targets with 5 MeV protons, and 5 MeV helium ions. The irradiation-induced formation rates of OCl^- and HOCl were determined by UV-Vis spectrophotometry. To give an example, the measured G values for the HOCl formation in 3.7 M $MgCl_2.6H_2O$, pH 4.42, irradiated by 5 MeV protons was determined to be 0.0374 ± 0.0022, and 0.0536 ± 49 by irradiating with 5 MeV helium. The distinguished knowledge about the radiation-induced production of oxo-chloride species is the first step towards the assumption of their steady-state concentrations in the irradiation field of the repository.

INTRODUCTION

Intrusion of a nuclear waste repository in deep salt formations may cause the repository to be inundated with brine from surrounding aquifers and the chloride brines to be exposed to radiation from the nuclear waste. The α-radiation emitted from light actinides contained in the waste (U, Np, Pu, Am and Cm) will induce the formation of

radiolysis by-products in the brine solution such as hypochlorite (OCl^-), hypochlorous acid (HOCl), hydrogen peroxide (H_2O_2). In the absence of reductants caused by iron corrosion for example, hypochlorite can cause high redox potential in brines, which may enhance dissolution rate of waste-forms, and oxidizes actinides to their highest oxidation state, which is usually the most soluble. Most of the elements are stable in one or two oxidation states, (U(IV,VI), Np(IV,V), Am (III, V), and Cm(III). In contrast, plutonium may exist in multiple oxidation states (III, IV, V, VI) simultaneously complicating the prediction of Pu speciation and concentration limits. Therefore, the radiolytically-induced redox reactions in concentrated saline solutions are of particular importance because the radiolysis of saline solutions results in oxidizing chlorine-containing species [1-6], which may oxidize actinide species to higher oxidation [7, 8]. To this point, irradiation effects on repository related materials using 4-6 MeV He-ions have been entirely performed on solid targets such as NaCl and $MgCl_2$ single crystal substrates. A comprehension of this field of research has been summarized by Tandon [9]. Helium ions in the MeV energy range as well as heavy noble gas ions (e.g. Xe^{2+}) in the 100 keV to MeV energy range have been introduced into solid targets to study irradiation damage effects and to determine susceptibility of different target materials (actinide host phases) to irradiation damage [10-12]. We have already simulated the effect of α-irradiation ion liquid media by treating 5*M* NaCl solution as well as 3.7*M* $MgCl_2.6H_2O$ and synthetic based $MgCl_2$ brine with 4.9 MeV protons [4-6]. The primary intention is to quantify the irradiation-induced formation of typical α-radiolysis by-product such a hypochlorous acid (HOCl) by UV Vis spectrophotometry, using He^{++} ions in the energy range of 4-6 MeV and to compare the dose related formation rates of a-radiolysis by-products (G value) assessed either by 4.9 MeV protons irradiation or 5 MeV He^{++} irradiation.

EXPERIMENTAL

The chemical reagents are purchased from Aldrich Chemicals suprapure (99.99%), and are used without further purification. The salt solutions 5 *M* NaCl, 3.7 *M* $MgCl_2.6H_2O$ are prepared by dissolving the proper reagent grade chemicals in distilled water. All experiments are carried out in glass vessels at 24 ± 2 °C under normal atmosphere. The pH is measured during the experiment using a combination glass electrode (Ross type, Orion Co). This set of experiments is designed to (1) assess if either OCl^- or HOCl can be formed directly by applying He^{++} ion-beam experiment, and (2) determine the irradiation induced HOCl/OCl^- formation as a function of the absorbed irradiation dose using a 20 mL test cell, attached to the 3 MV Tandem ion accelerator via a doubled-window interface [5]. This doubled window consists of a 10 μm Harvar® foil to seal the high vacuum of the beam-line and a 8 μm Kapton® foil as a membrane towards the test cell. The experimental details are displayed in Tables I.

Table I: Experimental details for the liquid-cell test experiment: Irradiation-induced hypochlorous acid formation in 20 mL 3.7 *M* $MgCl_2.6H_2O$ solution using proton and helium ions irradiation.

Target	3.7 *M* $MgCl_2.6H_2O$ pH 4.42 4.9 MeV Protons Irradiation	3.7 *M* $MgCl_2.6H_2O$ pH 5.072 5.2 MeV He^{++} ions Irradiation
Ionic strength	3.7	3.7
Chloride concentration (mol/L)	7.4	7.4
Mass to be irradiated (kg)	$2.50x10^{-2}$	$2.50x10^{-2}$
Source energy after acceleration (eV)	$5.50x10^{6}$	$8.80X10^{6}$
Energy (eV) after the UHV window (Harvar® 10 μm)	$5.022x10^{6}$	$6.030x10^{6}$
Energy (eV) after test-cell window (Kapton® 8 μm)	$4.935x10^{6}$	$5.164x10^{6}$
Total cumulative energy (J)	177.6	278.9
Total introduced dose (kGy)	7.10	11.15

The salt solution was irradiated using a similar approach described in [3, 5, 6]. After introducing 6 μC of 5.2 MeV He^{++} ions source or 4.9 MeV protons source into the liquid cell, a UV Vis absorption spectrum (Spectrophotometer Shimadzu Multispec 1501) of the irradiated chloride solution is taken to determine the progress of radiolysis by-products formation, knowing that HOCl spectroscopic characteristics in 3.7 *M* $MgCl_2.6H_2O$ at pH 4.42 [6] are: (1) absorption band at 232 nm, and (2) molar extinction coefficient ε 13044 $L.mol^{-1}.cm^{-1}$. Each incremental irradiation step of 6 μC of 5.2 MeV He^{++} ions or 6 μC of 4.9 MeV protons is associated with 30.983 J energy or 29.633 J energy respectively increasing the absorbed irradiation dose in the test cell by approximately 1.2 to 1.25 kGy. In this experimental set-up, total absorbed doses up to 14.87 kGy were introduced.

We used Monte Carlo simulation (SRIM) [13] for information on (1) the stopping of 4.9 MeV protons and 5.2 MeV He^{++} ions in 3.7 *M* $MgCl_2.6H_2O$, as well as (2) the associated ionization of the constituents in this salt solution. Primary 5.2 MeV He^{++} ions

irradiation-brine interaction is limited to the first 35.4 μm layer of the 20 mL brine salt solution, situated just behind the 8 μm Kapton® window (Fig. 1).

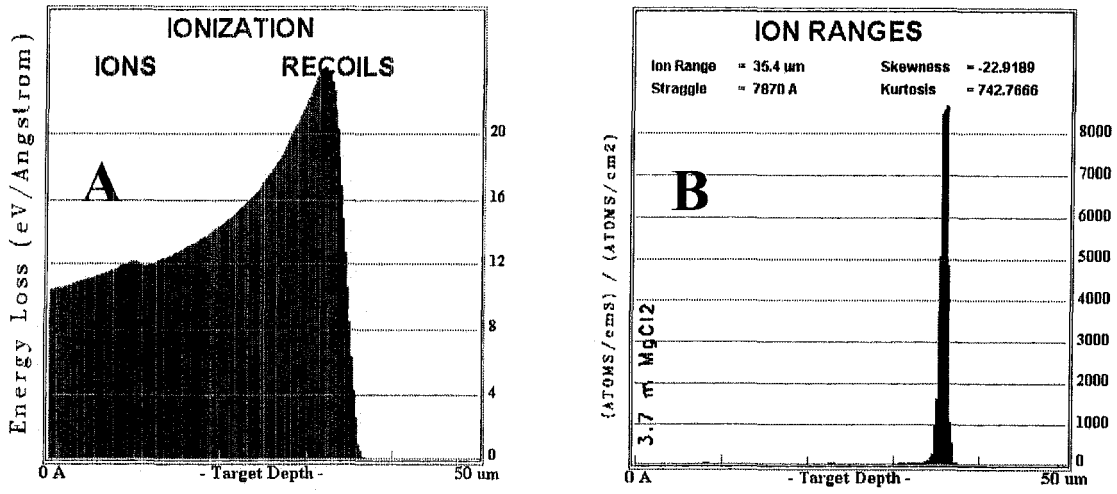

Fig. 1: The Monte Carlo Simulation (SRIM) of the collision events within the liquid cell towards the beam-line: (A) Ionization of the constituents in 3.7 *M* $MgCl_2.6H_2O$ solution by irradiating with 5 MeV He^{++} ions, (C) Ion ranges of 5 MeV He^{++} ions in 3.7 *M* $MgCl_2.6H_2O$ solution: 35.4 μm.

RESULTS AND DISCUSSION

The irradiation of 3.7 *M* $MgCl_2.6H_2O$, by 4.9 MeV protons up to doses of 7 kGy as well as by 5.2 MeV He^{++} ions up to doses of 14 kGy lead to the formation of hypochlorous acid (HOCl) determined spectrophotometrically at 232 nm (Fig. 2).

As a comparison, the UV Vis absorption spectrum of the individual species ClO^-, Cl_3^- in 3.7 *M* $MgCl_2.6H_2O$, is plotted in Fig. 3 as a function of pH, in the wavelength range of 190 nm to 400 nm. The generation of Cl_3^- is well recognizable by its broad absorption band at 325 nm, while hypochlorite ion ClO^- exhibits a peak shifted towards lower wavelength at 282.7 nm (ε= 197 $L.mol^{-1}.cm^{-1}$), the concentration of hypochlorous acid (HOCl) is in a steady-state at micromolar-level in the pH range 4 to 6 with a molar extinction coefficient ε= 13044 $L.mol^{-1}.cm^{-1}$ [5,6].

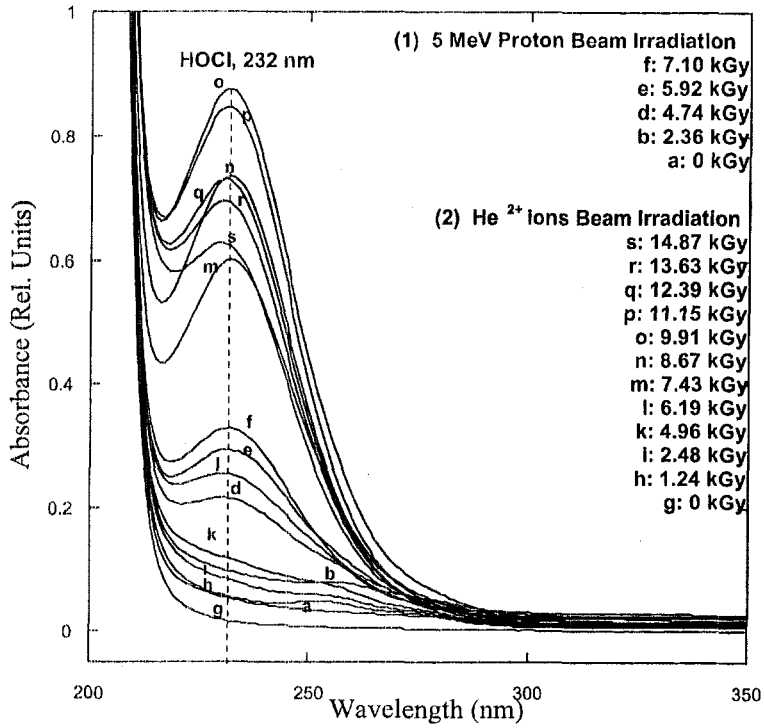

Fig. 2: UV Vis absorption spectra of 3.7 *M* $MgCl_2.6H_2O$ irradiated by (1) 4.9 MeV protons source, pH = 4.42, (2) 5.2 MeV He^{++} ions source, pH = 5.072

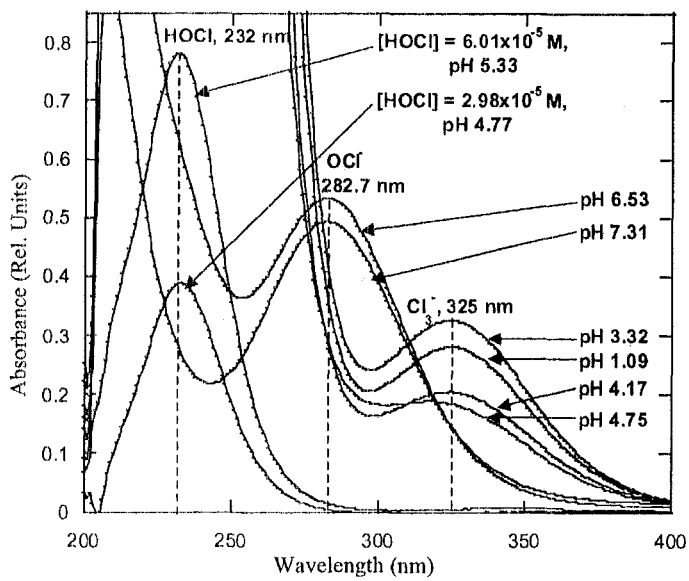

Fig. 3: UV Vis absorption spectra of chloride species in 3.7 *M* $MgCl_2.6H_2O$

To simulate the effects of Pu self-irradiation on repository related chloride solutions, we irradiated 3.7 *M* $MgCl_2.6H_2O$ solution by 5.2 MeV He^{++} ions with incremental steps of 1.2 kGy to reach a final absorbed irradiation dose of 14.87 kGy. To monitor the formation of HOCl, a UV Vis absorption spectrum was taken after each irradiation step (Fig. 2). The spectrum at 0 Gy irradiation represents the non-irradiated 3.7 *M* $MgCl_2.6H_2O$ solution. The formation of ClO_2^-, as an intermediate species, is observed at 256 nm for both irradiation sources 4.9 MeV protons as well as 5.2 MeV He^{++} ions. The concentration of chlorite ion can be assumed to be in the micromolar concentration range. After introducing 4 kGy with 5.2 MeV He^{++} ions source, the chlorite species has mainly disappeared and the formation of HOCl is observed and associated with a peak at 232 nm which was confirmed in parallel experiments by adding hypochlorous acid to a 3.7 *M* $MgCl_2.6H_2O$ solution [5,6]. The progress of HOCl production is not directly proportional to the dose, it more likely shows an alternation overlaying an overall linear growth like the one that was observed with 4.9 MeV protons irradiation (Fig. 5) [5]. The highest HOCl concentration formed after introducing 8.67 kGy dose in 3.7 *M* $MgCl_2.6H_2O$ solution, was determined to be 66.7 µmol HOCl based on the molar extinction coefficient of 13044 $L.mol^{-1}.cm^{-1}$ at 232 nm. However, these short-term and unique irradiation experiments demonstrate that the radiation-induced formation of hypochlorous acid is activated by rather low absorbed doses. We can estimate the formation rate of hypochlorous acid depending on the medium using He^{++} ions irradiation or protons irradiation (Fig. 5, linear fit).

The measured G-value for HOCl formation in a 20 mL quartz cell containing 3.7 *M* $MgCl_2.6H_2O$ solution, pH 4.42, irradiated by protons is estimated to be 0.0374 ± 0.0022 molecules /100 eV, while irradiated by helium ions G(HOCl) is estimated to be 0.0536 ± 0.0049 molecules /100 eV. (Tables II).

Table II: G(HOCl) value for 3.7 *M* $MgCl_2.6H_2O$

	4.9 MeV protons irradiation	5 MeV He^{++} ions irradiation
[HOCl] (mmole/kGy)	0.00388 ± 23	0.00556 ± 51
Sample Mass (kg)	0.025	0.025
Dose per µC (Gy)	$1.97 \cdot 10^2$	$2.06 \cdot 10^2$
Target Energy (eV)	$4.935 \cdot 10^6$	$5.164 \cdot 10^6$
$G_{(HOCl)}$ (number of HOCl molecules formed per 100 eV)	0.0374 ± 0.0022	0.0536 ± 0.0049

We have quantified previously the formation of hypochlorite at rather low dose and dose rate. The measured G-value for ClO^- formation in a 20 mL quartz cell containing 5 *M* NaCl solution, irradiated by proton ions has been estimated to be 0.0949 molecules /100 eV [3], which is in good agreement with the data published by Kelm et al. [2] of 0.0965 for alpha-self-irradiation using plutonium solutions of 37 GBq/L. If no decomposition of hypochlorous acid is considered, the hypochlorous acid concentration will reach saturation as the result of the combination of irradiation induced formation and energy-triggered disintegration of hypochlorous acid. The final steady-state concentration of hypochlorous acid will mainly depend on several criteria: (1) the applied

dose rate (kGy/h) as well as (2) the presence of constituents (metals) which could enhance the decomposition of hypochlorous acid.

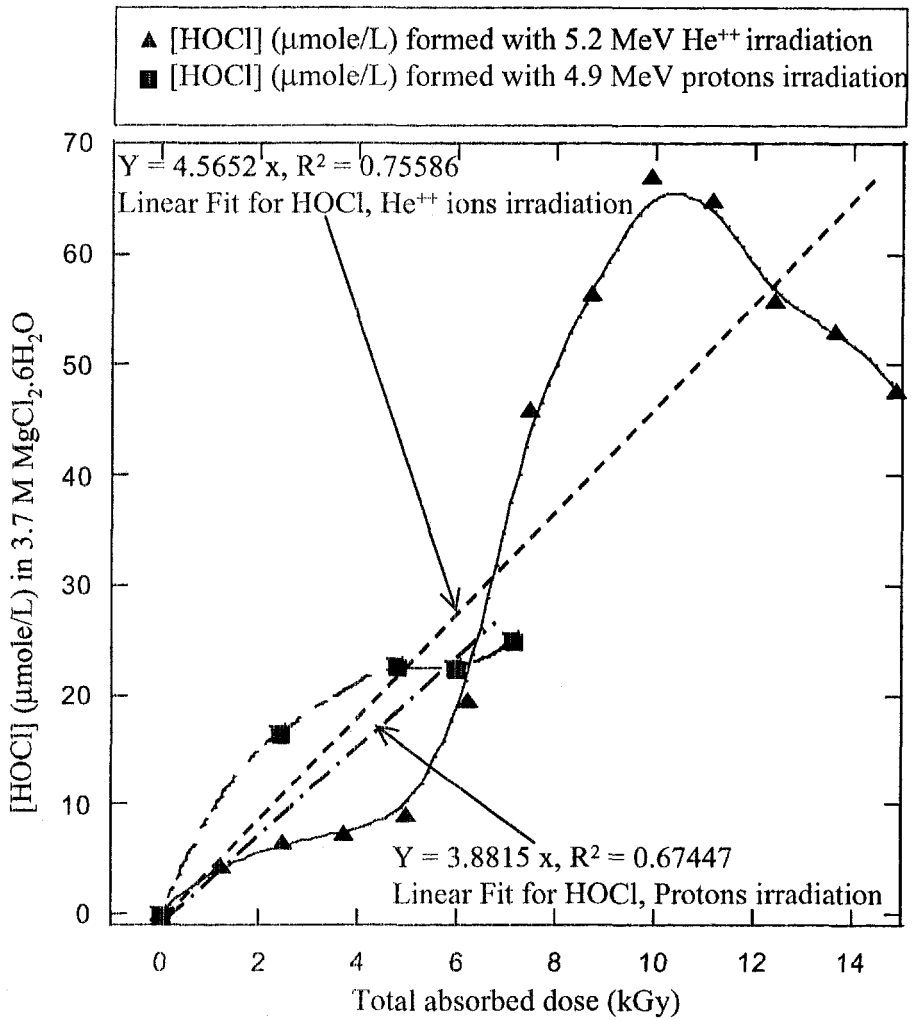

Fig. 4: Protons- and Helium ions-irradiation-induced hypochlorous acid formation as a function of total absorbed dose while irradiating 20 mL of 3.7 *M* $MgCl_2.6H_2O$ with 4.9 MeV proton ions or 5.2 MeV He^{++} ions.

CONCLUSION

By conducting this new and unique experimental approach, we demonstrate that applying non-radioactive beam-line experiments is durable to generate valuable data on the formation of radiolytical constituents. The formation rates of radiolytical species are important to understand impact of the radiation induced on the long-term geochemistry of a nuclear salt repository. In current geochemical models which also assess the actinide solubilities under the individual repository conditions, steady-state concentration of radiolytical species such as hypochlorite and hypochlorous acid are not considered for

now, because radiolysis taking place in a salt repository after water intrusion and waste-forms corrosion is not fully understood yet. At the current state of our experiment, we can directly determine the irradiation-induced formation of hypochlorite and hypochlorous acid as a function of absorbed dose. The measured G-value for HOCl formation in a 20 mL quartz cell containing 3.7 *M* $MgCl_2.6H_2O$ solution, pH 5.072 irradiated by 5.2 MeV He^{++} ions is estimated to be 0.0536 ± 0.0049 molecules /100 eV, while the measured G-value for HOCl formation in a 20 mL quartz cell containing 3.7 *M* $MgCl_2.6H_2O$ solution, pH 4.42 irradiated by 4.9 MeV protons is estimated to be 0.0374 ± 0.002. molecules /100 eV. In real groundwaters, the situation will get even more complex with the presence of metal corrosion constituents, which may partly catalyze the decomposition of radiolytical products such as HOCl. It has to be pointed out, that beam-line experiments on non-active samples as performed here, mainly focus on radiolytical formation rate rather than the determination of steady-state concentrations. In this four hours-experiment, we were able to determine the total formation of radiolytical species formed in a salt repository within one to two years after complete degradation of the waste-forms and their inundation in chloride brines.

REFRENCES

1. Kelm M., Bohnert E., *Radiolytic compounds formed by dissolution of irradiated NaCl and $MgCl_2.6H_2O$ in water.* Radiochim. Acta, **74**,155, 1996.
2. Kelm M., Pashalidis I., Kim J.I., *Spectroscopic investigation on the formation of hypochlorite by alpha radiolysis in concentrated NaCl solutions,* Applied Radiation and Isotopes, **51**, 637, 1999.
3. Hartmann T., Wetteland C., Ware D., Lu N., Sage S., Walthall M., Moir D., Paviet-Hartmann P., *Spectroscopic investigation of the formation of hypochlorite, radiolysis by-products in 5 M NaCl featuring high-energy proton beam line experiments*, Proc. Spectrum 2002, Int. Conf., Reno, NV, USA, August 4-8, 2002, LANL report LAUR-02-2261, Los Alamos National laboratory.
4. Paviet-Hartmann P., Dziewinski J., Hartmann T., Marczak S., Lu N., Walthall M., Rafalski A., Zagorski Z.P., *Spectroscopic investigation of the formation of radiolysis by-products by 13.9 MeV linear accelerator of electrons (LAE) in salt solutions*. Proc. Waste Management '02, Int. Conf., Tucson, AZ, USA, February 24-28, 2002, LANL report LAUR-01-6300, Los Alamos National Laboratory.
5. Hartmann T., Wetteland C., Ware D., Lu N., Sage S., Walthall M., Paviet-Hartmann P., *Spectroscopic investigation of the formation of α-radiolysis by-products in chloride brines featuring high-energy proton beam line experiments*, 224th ACS meeting, August 18-22, 2002, Boston, MS, LANL report, LAUR-02-3501, Los Alamos National Laboratory.
6. Hartmann T., Paviet-Hartmann P., Wetteland C., Lu N., *Spectroscopic determination of the formation of hypochlorous acid, in chloride brine solutions, featuring 5 MeV proton beam line experiments.* Submitted to Rad. Phys. Chem.
7. Magirius S., Carnall W., Kim J.I., *Radiolytic oxidation of Am(III) to Am(V) in NaCl solutions.* Radioachim. Acta, **38**, 29, 1985.

8. Kim J.I., Lierse C., Büppelmann K., Magirius S., *Radiolitically induced oxidation reactions of actinide ions in concentrated salt solutions.* Mat. Res. Soc. Symp. Proc., **84**, 603, 1987.
9. Tandon L., *Radiolysis of Salts and Long-Term Storage Issues for Both Pure and Impure PuO_2 Materials in Plutonium Storage Containers.* 2000, *LANL Report: LA-13725-MS*
10. Ewing R.C., Weber W.J., Clinard Jr F.W., *Radiation Effects in Nuclear Waste Forms for high level Radioactive Waste.* Progress in Nuclear Energy, **29**, 63, 1995.
11. Sickafus K.E., Minervini L., Grimes R., Valdez J., Ishimaru M., Li F., McClellan K., Hartmann T., *Radiation Tolerance of Complex Oxides,* Science, **289**, 748, 2000.
12. Hartmann T., Wang L., Weber W., Yu N., Sickafus K.E., Mitchell J., Wetteland C., Nastasi M., Hollander M., Baker N., Evans C., Tesmer J., Maggiore C., *Ion Beam Radiation Damage Effects in Rutile (TiO2).* Nuclear Instruments and Methods in Physics Research, **B 141**, 398, 1998.
13. Ziegler J.F., Biersack J.P., Littmark U., *The Stopping and Range of Ions in Solid.* Pergamon PressNew York, 1996.